



Oxidant free one-pot transformation of bio-based 2,5-bis-hydroxymethylfuran into α -6-hydroxy-6-methyl-4-enyl-2H-pyran-3-one in water

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ABSTRACT

A new synthetic route for obtaining α -6-hydroxy-6-methyl-4-enyl-2H-pyran-3-one, a useful synthon for the preparation of biologically active compounds, has been developed from the bio-based platform derivative (2,5-bis-hydroxymethylfuran) BHMF. The reaction occurs with good selectivity in water, under mild conditions and employing an heterogeneous recyclable acid (Amberlyst 15[®]) as catalyst, avoiding the use of oxidizing agents. The reaction provides access to poly-oxygenated compounds characterized by a molecular motif commonly found in many natural products.

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1. Introduction

Biomass and biomass-derived chemicals hold promise in transitioning to a more sustainable bio-based economy based on a new portfolio of products that have no equivalence to those presently manufactured by classical synthesis routes from hydrocarbons [1–14]. In particular, furans (e.g., 5-hydroxymethylfurfural HMF) are important biomass-derived molecules which can be used as starting materials for the synthesis of a variety of potentially useful compounds [15]. The structural moieties present in HMF, allow synthetic transformations to other target molecules by means of selective reactions such as: oxidation of the formyl group [16–23], reduction of the formyl group and/or the furan ring [24–25], deoxygenation of the hydroxyl groups to 2,5-dimethylfuran [26–29], etherification and carbonylation [30–35], and hydrogenolysis transformations [36–37]. In particular, selective reduction of 5-hydroxymethylfurfural (HMF) provides access to the diol 2,5-bis-hydroxymethylfuran (BHMF), a valuable build-

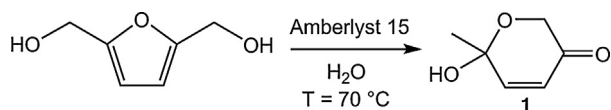
ing block for the production of polymers and polyurethane foams [18,38,39]. HMF reduction to BHMF can be performed under stoichiometric conditions in the presence of NaBH₄ [40–42] or by using aqueous solutions of HCHO and NaOH [43], in the presence of catalysts such as: copper chromite [44], Ni Raney [45], Pt-, Pd- or Ru-supported catalysts [26,46–48]. Main drawbacks are the toxicity of some of the catalysts employed, and the high temperature (140–200 °C) and pressure (70–75 bar) required [5].

Recently our group has developed a new process for the selective and quantitative reduction of HMF to BHMF exploiting the well-known Shvo catalyst [49]. Herein, we report on further transformation of BHMF into α -6-hydroxy-6-methyl-4-enyl-2H-pyran-3-one upon treatment with an heterogeneous acid catalyst (Amberlyst 15[®]) in water and in the absence of oxidizing agent. The same treatment in alcohol lead to etherification of the OH functionalities and no rearrangements are observed [50–51]. Amberlyst 15[®] is non-hazardous in nature and easily separable from reaction mixture, on the basis of its physical properties such as high H- exchange capacity (4.7 meq/g) and surface area (42 m²/g) it combines very useful acidic properties, with benign environmental character, reusability and commercial availability [52–54]. The present reaction is consistent with most requirements typical of green methodologies, in that it is atom economic [55], one-pot reaction [56] and performed in water as solvent [57], with the pos-

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Scheme 1. Reaction of BHMf in water with Amberlyst 15® ($t = 30$ min; $T = 70$ °C, $H_2O = 20$ mL).

sibility to recycle the catalyst. Furthermore, the product obtained represents an attractive synthon for the preparation of sugar analogues and compounds showing biological activity [58–66].

2. Experimental section

2.1. Materials

Solvents: water has been freshly distilled; diethylether, methanol (MeOH), $CDCl_3$, CD_3CN , D_2O (Sigma–Aldrich), reagents: H_2SO_4 , HCl, furfuryl alcohol (Sigma–Aldrich), 5-hydroxymethylfurfural (HMF) (SAFC), and resins Amberlite IRC50®, Amberlyst 15® wet, Amberlyst 70® have been employed as purchased, 2,5-bis(hydroxymethyl)furan (BHMf) has been prepared as described in the literature [49].

2.2. Analytical methods

The NMR spectra were recorded using Varian Inova 300 (1H , 300.1; ^{13}C , 75.5 MHz), Varian Mercury 400 (1H , 399.9; ^{13}C , 100.6 MHz), Varian Inova 600 (1H , 599.7, ^{13}C , 150.8 MHz) spectrometers. Infrared spectra were recorded at 298 K on a PerkinElmer Spectrum 2000 FT-IR spectrophotometer. GC analyses have been performed on an Agilent Technologies 6890N instrument (column: agilent 19091J-433HP-5). HPLC analyses were performed on an Agilent Technologies 1260 infinity instrument, equipped with a C-18 core shell column 50×4.6 mm employing a solution of 80% of 0.01 M H_3PO_4 and 20% acetonitrile as mobile phase. Particular care was devoted to estimate of the C balance, which was found to always fall between 95 and 105% (calculated as the comparison between converted BHMf and product yields) unless in the presence of unidentified by-products.

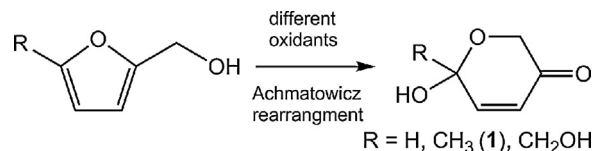
2.3. BHMf rearrangement

2.3.1. Amberlyst 15®

BHMf (54.8 mg, 0.43 mmol) is dissolved in a suspension of Amberlyst 15® (256 mg) in water (20 mL). For reactions performed under nitrogen atmosphere the aqueous suspension of Amberlyst 15® is degassed and purged with nitrogen. The mixture is warmed to the desired temperature and the suspension maintained under stirring for the time requested and then cooled in a water bath. The catalyst is filtered off and the solvent removed under vacuum (at a temperature lower than 40 °C). The reaction crude is analysed by GC–MS, 1H and ^{13}C NMR and HPLC. From those analyses the following products are identified in variable mixtures. BHMf, α -6-hydroxy-6-methyl-4-enyl-2H-pyran-3-one (**1**), 1,3-dihydroxyhexan-2,5-dione (**2**), 1,4-dihydroxyhexan-2,5-dione (**3**). For recycling experiment the Amberlyst 15® has been dried at 65 °C for 14 h before used for further runs.

2.3.2. HCl or H_2SO_4

BHMf (54.8 mg, 0.43 mmol) is dissolved in a water (20 mL) solution of the desired quantity of HCl or H_2SO_4 . The reaction mixture is stirred at 70 °C for 30 min. Then it is cooled to room temperature and neutralized with NaOH. Water is removed under vacuum and the crude dissolved in CH_2Cl_2 . After anhydrication on Na_2SO_4



Scheme 2. Some example of Achmatowicz rearrangement.

the solution is filtered and the solvent removed under vacuum. The crude has been analyzed by 1H NMR.

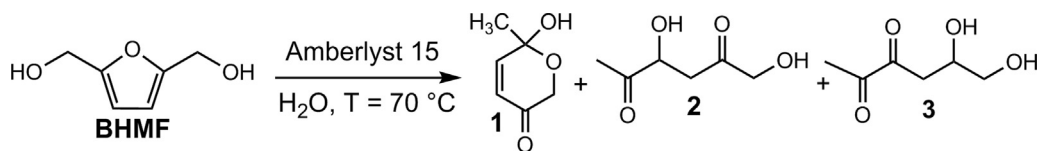
3. Results and discussion

3.1. Catalyst screening

The substrate BHMf has been treated in the presence of different heterogeneous acid catalysts such as Amberlite IRC50®, Amberlyst 15® and Amberlyst 70®. Amberlite IRC50® did not produce any conversion of BHMf at 100 °C, even upon different catalyst loading (up to 1 $g_{CAT}/mmol_{BHMf}$). Concerning the reaction with Amberlyst 15®, no conversion occurred with 0.1 $g/mmole_{BHMf}$, while with a loading of 0.8 $g_{CAT}/mmole_{BHMf}$ decomposition of BHMf was detected by the formation of an insoluble black product. Lowering the catalyst/substrate ratio to 0.5 $g_{CAT}/mmole_{BHMf}$, a complete conversion of BHMf was observed within 30 min at 70 °C, leading to the formation of a mixture of products. The high catalyst loading (actually one H^+ sites each BHMf) suggests that a high acid content for the catalyst is required in order to promote the reaction; moreover, the inactivity of Amberlite IRC50® (carboxylic vs. sulfonic acid, and 0.43 meq H^+/g vs. Amberlyst 15® 4.7 meq H^+/g) points out for the need of a strong acidity. 1H NMR and ^{13}C NMR (g-HSQC e g-HMBC) allowed the identification of α -6-hydroxy-6-methyl-4-enyl-2H-pyran-3-one (**1**) (Scheme 1) as major product. Under the same reaction conditions Amberlyst 70® (2.55 meq H^+/g) leads to complete conversion of BHMf, but with a lower selectivity (<38% in **1**). Indeed, compound **1** became the minor product suggesting that, besides the amount of acidic sites a specific role seems to be played by the nature and texture properties of the resin. The latter behavior, unexpected because of the lower acidity of Amberlyst 70® compared to Amberlyst 15®, can be explained considering a different diffusion of the substrate in the pore of the resins. Performing an absorption experiment at room temperature (54.8 mg BHMf, 20 mL H_2O [BHMf = 22 mM], r.t., 1 h, 0.256 mg Amberlyst 15® or 70®) the concentration in BHMf in solution at the end of the experiment resulted lower in the case of Amberlyst 70® (17 mM vs 19 mM for Amberlyst 15®). This effect is similar to that reported in literature for zeolites, which can selectively extract a component of the reaction mixture exploiting their hydrophilic/hydrophobic characteristics. This effect is particularly evident when the reaction is performed in polar solvents such as water [67].

The 1H NMR signals, assigned to the pyranone **1** (Fig. S4), are consistent with those reported for the same product obtained by a different synthetic approach [68], better known as the Achmatowicz rearrangement [69] which is the oxidative rearrangement of 2-(α -hydroxyalkyl) furan, to form 6-hydroxy-3(2H)-pyranones (Scheme 2). The Achmatowicz rearrangement occurs under a variety of conditions, including treatment with: $Br_2/MeOH$ [69], peracids (e.g., m-CPBA [70], magnesium monoperoxyphthalate [71]), NBS [72], dioxiranes (DMDO [73]), metal-based oxidations (PCC [74], $VO(acac)_2/t-BuOOH$ [75] and titanium(IV) silicalite (TS-1)/ H_2O_2 [76]).

Analogies between the reaction of BHMf (Scheme 1) and the Achmatowicz rearrangement are obviously based on the similar nature of the pyranone products. However, there are relevant and peculiar differences, in that our reaction provides



Scheme 3. Reaction conditions: 0.5 g_{CAT}/mmol_{BHMf}, N₂, degassed water, 70 °C, *t* = 30 min.

Table 1

Acid catalyzed BHMf conversion to **1**. Reaction conditions: 0.5 g_{CAT}/mmol_{BHMf}, *t* = 30 min.

Entry	Atmosphere	<i>T</i> (°C)	Conversion (%)	Yield (%)	Selectivity (%)
1	Air	70	91	45	49
2	N ₂	70	76	50	70
3	N ₂	50	12	5	46
4	N ₂	90	>99	0	0

access to **1** without requiring oxidants. On the other hand, the Achmatowicz rearrangements as shown in Scheme 2 do not take place when the reactions occur under the conditions as shown in Scheme 1. For example, treatment of furfuryl alcohol with Amberlyst 15[®] (0.5 g_{CAT}/mmol_{Furfuryl alcohol}, H₂O 20 mL, *T* = 70 °C, *t* = 30 min) does not lead to the formation of pyranone products. A further observation is that BHMf, under Achmatowicz conditions is transformed into a more oxidized product (see Scheme 2, R = CH₂OH), compared to **1**, which is instead obtained from 2-methyl-5-hydroxymethylfuran. It has to be underlined that the number of methods developed to undertake the oxidative Achmatowicz rearrangement accounts for both the usefulness 6-hydroxy-3(2H)-pyranones, and the lack of a single, very effective and reliable synthetic route. Methods proposed so far exhibit limits mostly arising from the harshness of the reaction conditions and the lack of selectivity associated. Drawbacks include tedious work-up, use of expensive reagents or high energy-demand, non-scalability, formation of salt waste or low catalyst recyclability. For example, although the NBS and peroxyacid mediated reactions usually offer simple procedures, it was found that these methods are unreliable and unsuitable for all but very small-scale work. On the other hand, the bromomethoxylation procedure is highly sensitive to temperature and produces stoichiometric amounts of NaBr. In contrast to the above-mentioned methods, using TS-1 as a heterogeneous catalyst and aqueous H₂O₂ as an inexpensive oxygen source, small-sized furfuryl alcohols are readily converted into 6-hydroxy-2H-pyran-3(6H)-ones with high yield and high oxidant efficiency. Moreover, the use of other Ti-substituted molecular sieves possessing larger pores, such as zeolite Ti-Beta or mesoporous Ti-MCM-41, provide access to the oxidation of more bulky furfuryl alcohols [77–78]. More recently, it has been reported a greener method based on non-toxic singlet oxygen (¹O₂), run in MeOH in the presence of a reducing agent [79], and in water exploiting light and spirulina as the photosensitizer [80]. In our reaction, the presence of two hydroxyl groups on the furan ring makes the oxidant source unnecessary, and results in a greener approach to pyranones.

3.2. Screening of the reaction conditions

The reaction has been performed also under nitrogen atmosphere. Both GC–MS and NMR spectra (¹H and ¹³C NMR) confirm the formation of α-6-hydroxy-6-methyl-4-enyl-2H-pyran-3-one (**1**) as well as of the by-products 1,3-dihydroxyhexan-2,5-dione (**2**) and 1,4-dihydroxyhexan-2,5-dione (**3**). (Scheme 3 and Fig. S6).

As reported in Table 1 the reaction under nitrogen atmosphere (entry 2) shows a better selectivity in the formation of **1** than in the presence of air (entry 1). Comparison of the NMR spectra of the

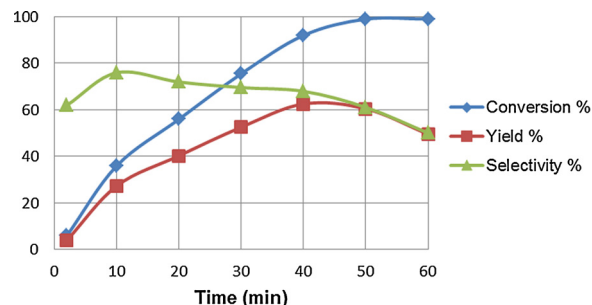


Fig. 1. BHMf conversion, yield and selectivity of **1** in function of time. Reaction conditions: 0.5 g_{CAT}/mmol_{BHMf}, *T* = 70 °C, under N₂.

reaction mixture obtained under air (Fig. S4) and inert atmosphere (Fig. S5), evidences that the main products are the same in both the cases: **1**, **2**, and **3**. However, in the presence of air, some unresolved signals, indicative of lower selectivity, were also observed. For those signals assignment was not possible with information in our hands. The reaction is supposed to be the same in both cases and no oxidation is expected in the presence of the sole oxygen from air. It is worth noting that lower temperatures (e.g., 50 °C, entry 3) have a detrimental effect on both yield and selectivity. The same negative behavior is observed at higher temperatures: at 90 °C (entry 4), although BHMf completely converts, no selectivity in the desired product **1** is observed. Product **1** has been purified by column chromatography on deactivated silica (treated with a Et₂O solution of NEt₃). The product was eluted with Et₂O and isolated with a 25% yield.

Unfortunately carrying out the reaction at higher concentrations (e.g., 2 mL of H₂O and 4 mL of H₂O; Amberlyst 15[®], 0.5 g_{CAT}/mmol_{BHMf}, N₂, degassed water, 70 °C, *t* = 30 min) lead to complete conversion but to null selectivity. Finally the reaction behavior in function of the reaction time is reported in Fig. 1. The reaction reaches complete conversion within 60 min and the selectivity results lower than 100% already at the beginning of the reaction suggesting that a parallel reaction is involved, with formation of the side products **2** and **3**.

3.3. Catalyst recycling

The resin employed under the reaction conditions of Table 1 – entry 2 (*T* = 70 °C, *t* = 30 min) was washed with water and dried at 65 °C for 14 h, then was further employed for recycling tests maintaining the same activity for four cycles (Fig. 2). FT-IR (KBr) analysis of the resin before and after use and comparison with the spectra of BHMf and **1** indicates that neither reagents nor products remain absorbed over the resin.

3.4. Reaction mechanism

Based on the nature of the reaction products and on what reported for furan hydrolysis [25,81] and for Achmatowicz reaction [42,76,79] a tentative reaction mechanism has been depicted (Scheme 4). It consists of an hydration of one C=C double bond of BHMf followed by a dehydration that involve the hydroxymethyl group on the other side of the ring. Then

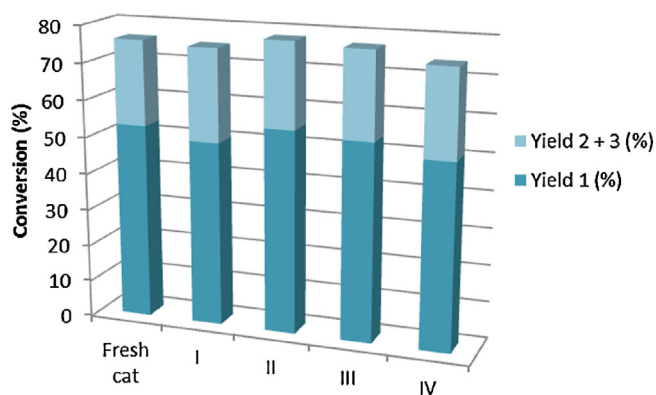


Fig. 2. Recycling of Amberlyst 15[®]. Reaction conditions: 0.5 g_{CAT}/mmol_{BHMF}, $T = 70^\circ\text{C}$, $t = 30\text{ min}$, under N_2 .

the ring of 2-hydroxymethyl-5-methylen-2,5-dihydrofuran-2-ol undergoes ring opening giving rise to a keto-enol equilibrium. When the linear molecule is in its ketonic form a nucleophilic attack of the hydroxyl group on the terminal carbon lead to the ring closure and to the formation of compound **1** which is the major compound. The side products **2** and **3** are likely derived from parallel hydration of the ketonic intermediate before ring closure. However following the reaction up to 5 h the complete conversion of the product **1** into **2** and **3** is observed (GC–MS e ^1H NMR) that means that a consecutive hydration/ring opening of compound **1** also contributes to the formation of **2** and **3**.

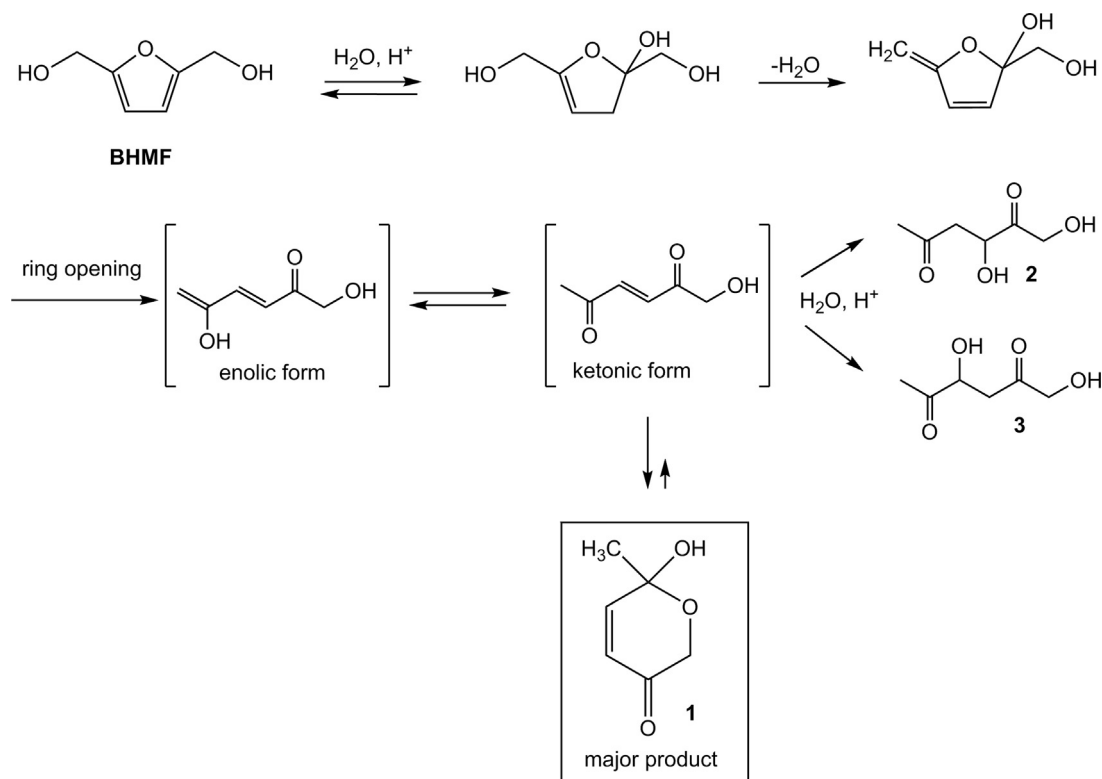
In order to validate the proposed mechanism the reaction has been also performed in D_2O with the same reaction conditions (0.5 g_{CAT}/mmol_{BHMF}; $T = 70^\circ\text{C}$, $t = 30\text{ min}$). ^1H NMR spectrum of the mixture shows the appearance of signals due to H/D coupling in the range in which signals attributable to CH_3 (δ 1.4–1.5 ppm) and to CH_2 (δ 2.0–2.2 ppm), which is consistent with the hydration and

dehydration steps in the proposed mechanism (see Scheme S1 and Fig. S9).

3.5. Homogeneous vs. heterogeneous acid catalysis

The reactivity of BHMF with an homogeneous acid catalyst (HCl) has been investigated in water at 70°C for 30 min by varying the solution pH (Table 2). The formation of a mixtures of compounds **1**, **2** and **3** with a general behavior similar to that found for the Amberlyst 15[®] resin (entry 1) is observed, however lower yields and selectivity in **1** are obtained in the case of the homogeneous system (HCl, entries 2–5). Data as shown in Table 2 also evidence that a low pH favors the conversion.

Employing H_2SO_4 instead of HCl as acid led to complete decomposition. The latter experiments confirm the role of acid in the formation of **1** from BHMF, as well as the need of a strong acidity in order to obtain complete conversion in due time (pH 1 for a complete conversion in 30 min). Moreover, the heterogeneous catalyst results, by far more effective in terms of selectivity, which is not obvious to explain. The heterogeneous catalyst might provide very high acid concentration, necessary to promote hydration-dehydration steps; however, the selectivity to **1** is determined by the relative ratio of the two parallel reactions leading either to **2** and **3** by hydration, or to **1** by cyclisation, both starting from the common precursor, the ketonic form of the intermediate compound (see Scheme 4). Furthermore by-products **2** and **3** can be obtained from the equilibrium between **1** and the ketonic form. Therefore some selectivity effect could be ascribed to the lower affinity of BHMF and/or **1** and/or the ketonic form for the acid sites in the case of Amberlyst 15[®], which favor the preferential formation of the desired product **1**, whereas Amberlyst 70[®] shows the preferred formation of **2**, **3** and of heavier compounds as well. Considering the acid sites of the Amberlyst 15[®] (4.7 meq/g) we can estimate a TON < 1 (0.36 under the hypothesis that all the acid sites are available for the reaction, which can give an underestimation of



Scheme 4. Proposed mechanism for the reaction of BHMF in water with Amberlyst 15[®]. Mechanism based on refs. [25,42,76,79,81].

Table 2
Reaction of BHMF with HCl at different pH.

Entry	Cat [H ⁺]	Conversion (%)	Yield of 1 (%)	Selectivity of 1 (%)
1	Amberlyst 15 [®] (0.5 g _{CAT} /mmol _{BHMF})	76	53	70
2	HCl (pH 1)	99	16	16
3	HCl (pH 2)	76	14	18
4	HCl (pH 3)	49	13	27
5	HCl (pH 4)	19	6	29

the TON) corresponding to a stoichiometric reaction rather than a catalytic one. In any case, the Amberlyst 15[®] can be recovered and reused with great advantages with respect to an unrecoverable homogeneous systems. Moreover, Amberlyst 15[®] has the most appropriate hydrophilic properties which both catalyze the hydration and dehydration of BHMF, and facilitate the cyclisation to yield the pyranone, by providing the proper balance between BHMF, water and acid sites concentrations.

4. Conclusions

In this novel and efficient acid-mediated BHMF rearrangement to α -6-hydroxy-6-methyl-4-enyl-2H-pyran-3-on in water neither ungreen oxidizing agents nor harsh conditions are required. The heterogeneous recyclable acid catalyst Amberlyst 15[®] allows good selectivity and mild conditions. The new method starts from a bio-based platform derivative such as BHMF and the protocol employs green, nontoxic reagents and conditions. Furthermore it is highly step-economic and highly efficient from the perspective of atom economy. The product obtained represents an attractive synthon for the preparation of biologically active compounds, making the protocol a step forward in the direction of the green approach to pharmaceuticals from biomasses. Mechanistic investigations open the street for the development of a general method for the transformation of variously functionalized dihydroxy-furans.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.01.029>

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